Global Crossover Peng-Robinson Equation of State

Kh. S. Abdulkadirova[†] and C.J. Peters
Institute for Geothermal Problems, Dagestan Scientific Center
of the Russian Academy of Sciences
Makhachkala 367030, Russia

M.A. Anisimov and J.V. Sengers
Institute for Physical Science and Technology and
Department of Chemical Engineering, University of Maryland
College Park, MD 20742 U.S.A.

The classical Peng-Robinson equation of state has been modified to incorporate the singular behavior near the critical point caused by fluctuations of density and classical regular behavior far away from the critical point. This goal is accomplished by applying a transformation deduced from the renormalization-group theory of critical phenomena for a classical Landau expansion of the Helmholtz energy [1] and improves upon a similar transformation of the van der Waals equation [2]. We have applied the crossover Peng-Robinson equation to methane and *n*-butane and explicitly demonstrated how the critical fluctuations change the classical near-critical behavior and how the 'classical' critical point drifts to its actual position. The fluctuations also change the shape of the coexistence curve near the critical point and lead to a singularity in the isochoric heat capacity. The crossover behavior is controlled by only one non-universal system-dependent parameter related to the range of intermolecular forces that can be found from experimental data. The crossover equation reduces to the classical Peng-Robinson equation far away from the critical point. It is important that the value of the compressibility factor Z_c of the crossover Peng-Robinson equation is equal to its experimental value.

[1] M.A. Anisimov, S.B. Kiselev, J.V. Sengers, and S. Tang, *Physica A* **188**, 487 (1992).
[2] A. Kostrowicka Wyczalkowska, M.A. Anisimov, and J.V. Sengers, *Fluid Phase Equil.* **158-160**, 523 (1999).

[†]Present address: Delft University of Technology
Faculty of Applied Sciences
Julianalaan 136, 2628 BL Delft, The Netherlands